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(54) Detergent compositions in tablet form.

(57) A product for treating fabrics in the washing machine is in the form of a tablet of compressed particulate bleaching composition comprising a persalt, preferably sodium percarbonate ; a bleach activator having an observed pseudo-first order perhydrolysis rate constant (K_{obs}) of from 1.5 x 10^{-4} to 350 x 10^{-4} sec^{-1}, for example, tetraacetylethylenediamine, glycerol triacetate, sodium benzoyloxy benzene sulphonate or 1-O-octanoyl-2,3-4,6-tetra-O-acetyl glucose ; and optionally detergent ingredients.

EP 0 481 792 A1

TECHNICAL FIELD

The present invention relates to a product for treating fabrics in the washing machine in the form of a tablet containing a particulate bleaching composition which may optionally include detergent ingredients.

BACKGROUND AND PRIOR ART

Detergent compositions in tablet form have been known for many years although the form has never achieved great popularity on the market. In principle, tablets offer several advantages over powder products: they do not require measuring and are thus easier to handle and dispense into the the washload, and they are more compact, hence facilitating more economical packaging and storage.

One difficulty that has been experienced in the formulation of detergent tablets is the incorporation of bleaching ingredients, especially when the presence of bleach-sensitive ingredients such as enzymes is also desired: in a compressed tablet, the ingredients are much more intimately associated with one another than in a powder, and any adverse interactions and instability will be exacerbated. Worse stability problems would be expected if bleach activators (bleach precursors) were present.

US 4 099 912 (Ehrlich) discloses a plurality of separate units of different detergent composition components which may be used in combination to obtain the required detergent formulation. Tablets are the preferred unit. A separate tablet containing sodium perborate or sodium percarbonate is suggested. Bleach activators are not mentioned.

GB 911 204 (Unilever) discloses layered detergent tablets containing persalt bleach, for example, sodium perborate, and certain bleach activators, for example, sodium acetoxybenzene sulphonate and phthalic anhydride. To avoid destabilisation, the bleach activator is segregated from the remaining tablet ingredients, including the persalt bleach, in a separate section or layer.

In contrast, EP 395 333A (Unilever) discloses a detergent tablet containing sodium perborate in conjunction with one or more bleach-sensitive ingredients - tetraacetylethylenediamine or similar bleach activator, enzyme, fluorescer, or any combination of these - as well as detergent-active compounds, detergency builders and optionally other ingredients. The persalt is not segregated from the bleach-sensitive ingredients but, surprisingly, the tablet is stable with no more loss of bleach, enzyme or fluorescer performance on storage than in a powder of the same composition.

It has now been discovered that tablets containing persalt bleaches and defined bleach activators together, in conjunction with detergent ingredients which are either present in the same tablet or in a separate tablet, or powder/liquid form, can give better bleaching performance than detergent powders of the same formulation. The benefits are especially evident when the persalt is sodium percarbonate and when the bleach activator is tetraacetylethylenediamine.

DEFINITION OF THE INVENTION

The present invention provides a tablet of compressed particulate bleaching composition comprising:

(i) a persalt;

(ii) a bleach activator having an observed pseudo-first order perhydrolysis rate constant (K_{obs}) of from 1.5 x 10^{-4} to 350 x 10^{-4} sec^{-1};

(iii) optionally a detergent-active compound;

(iv) optionally a detergency builder; and

(v) optionally other detergent ingredients;

with the proviso that if the persalt is sodium perborate and the bleach activator is a N-diacylated or N,N'-polyacylated amine, the persalt is segregated from the bleach activator.

Tablets in which sodium perborate and an N-diacylated or N,N'-polyacylated amine bleach activator are together without segregation are disclosed and claimed in the aforementioned EP 395 333A (Unilever) and are specifically disclaimed from the scope of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The tablet of the invention is characterised by the presence of both a persalt and a defined bleach activator. The interaction between the two bleaching components, to give better bleaching than the persalt alone can give, appears to be improved by tabletting.

Bleach activators work by reacting in the wash liquor with hydrogen peroxide from the persalt (perhydrolysis of the activator) to generate a peracid which is a more efficient bleach than is hydrogen peroxide itself. Without

limiting in any way the scope of the invention, it is hypothesised that in a porous tablet there is an opportunity for the activator to react with hydrogen peroxide from the persalt within the pores of the tablet itself, when the tablet first comes into contact with the wash liquor. In this confined space, the concentration of both hydrogen peroxide and precursor will be greater than in the bulk wash liquor, and the rate of perhydrolysis will be increased.

This can only occur, of course, if the tablet remains intact in the wash liquor for long enough for the reaction to take place to a significant degree. However, the peracid generated needs to be released into the wash liquor in order to reach the stain to be bleached, which requires the tablet to dissolve. A rate of tablet dissolution that represents an ideal compromise between these conflicting requirements is therefore desirable. A further requirement would appear to be that the tablet should remain porous enough under wash conditions to allow water to penetrate in sufficient quantity and with sufficient speed for reaction to take place. Rate of dissolution and tablet porosity will depend partly on formulation and may be also be controlled to some extent by choice of tabletting pressure.

The persalt

The most preferred persalt for use in the present invention is sodium percarbonate, although the use of other inorganic persalts, notably sodium perborate tetrahydrate is also within the scope of the invention.

Sodium percarbonate, $Na_2CO_3.1.5H_2O_2$, unlike sodium perborate, is a perhydrate rather than a true persalt, and it can release hydrogen peroxide of crystallisation without requiring dissolution. However, sodium percarbonate dissolves more slowly than sodium perborate monohydrate in water so that the tablet structure is maintained in the wash liquor for a sufficient length of time for the effect described above to operate.

Very little benefit has been observed with sodium perborate monohydrate, which dissolves very rapidly in water so that the tablet breaks up more quickly, but which requires an inherently slower reaction (hydrolysis) to release hydrogen peroxide.

Some benefit has been observed with sodium perborate tetrahydrate which is slower to dissolve than the monohydrate, but the effect is smaller than with sodium percarbonate.

The total amount of persalt in the tabletted composition as a whole is preferably within the range of from 5 to 60 wt%. In fully formulated detergent tablets the amount of persalt is preferably from 10 to 40 wt%, more preferably 10 to 30 wt%.

The bleach activator

The tablet of the invention also contains a defined bleach activator.

The extent to which the effect described above will operate will depend on the choice of bleach activator as well as on the choice of persalt. Preferably the activator is one having moderate reactivity, where the greatest improvement will be observed. Very fast reacting bleach activators will already perform so well that no further significant improvement is possible; while very slow reacting bleach activators will be improved but not necessarily to a sufficient extent to render them useful in practice.

It is thus an essential feature of the present invention for the bleach activator to have an observed pseudo-first order perhydrolysis rate constant (K_{obs}) of from 1.5×10^{-4} - 350×10^{-4} sec^{-1}. This rate constant provides a measure as to how reactive the bleach activator will be.

The best known bleach activators are peracetic acid precursors and perbenzoic acid precursors. The peracetic acid precursor, tetraacetylethylenediamine (TAED), is especially preferred for use in the tablets of the present invention because its reactivity is such that a particularly worthwhile improvement over loose powder can be demonstrated ($K_{obs} = 2.3 \times 10^{-3}$ sec^{-1}).

The peracetic acid precursor, glycerol triacetate, has also shown some benefit, but its reactivity is still rather low ($K_{obs} = 1.9 \times 10^{-4}$ sec^{-1}). Other peracetic acid precursors that would be expected to benefit from tabletting in accordance with the present invention include glucose pentaacetate and xylose tetraacetate.

An example of a perbenzoic acid precursor that may benefit from tabletting in accordance with the present invention is sodium benzoyloxybenzene sulphonate, although since this is already a fast-reacting precursor ($K_{obs} = 3 \times 10^{-2}$ sec^{-1}) the benefit is less substantial than with TAED.

Further examples of suitable precursors that may benefit from tabletting in accordance with the present invention are monosaccharide esters as disclosed in EP 0 380 437A (Procter & Gamble; Novo), and sugar ester-based precursors as disclosed in WO91/10719 (P&G; Novo) preferred compounds are 1-O-(long-chain acyl)-2,3,4,6-tetra-O-acetyl-glucose in α or β form where the long chain acyl is one of the following: octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, 10-undecanoyl, 3,5,5-trimethylhexanoyl or 2-ethylhexanoyl. The most preferred compound is where the long chain acyl is octanoyl: 1-O-octanoyl-2,3,4,6-tetra-O-acetyl-glucose

(OTAG).

Bleach activators are suitably present in an amount of from 1 to 30 wt%. In fully formulated detergent tablets the bleach activators are preferably present in an amount of from 1 to 10 wt%, more preferably from 2 to 5 wt%.

Bleach stabiliser

If desired, the tablet of the invention may also include a small amount of a bleach stabiliser (heavy metal sequestrant) such as ethylenediamine tetraacetate (EDTA), ethylenediamine tetramethylene phosphonate (EDTMP) or diethylenetriamine pentamethylene phosphonate (DTPMP).

Other ingredients

As well as persalt and bleach activator, the tablet of the invention may optionally contain at least one detergent-active compound, at least one detergency builder, and other ingredients. Tablets of the invention may therefore provide a fully formulated, high performance detergent composition within a single tablet. It is preferred, however, that a detergent composition consists of at least a two-tablet system; one, a tablet of the invention, containing the bleaching composition, the other containing the detergent base composition. Alternatively the detergent composition may consist of a tablet of the invention, containing the bleaching composition, and a power/liquid containing the detergent base composition.

Percarbonate segregation

If sodium percarbonate is present, it is preferably separated from any other ingredient likely to destabilise it by segregation in a discrete region of the tablet, as described and claimed in our copending British application No 90 22724.0 (Unilever PLC), filed 19 October 1990. This is particularly important when tablets which contain a full detergent composition within a single tablet are formulated.

According to British Application No 90 22724.0, at least one discrete region comprising sodium percarbonate and optionally other ingredients compatible with sodium percarbonate is present. Other components such as detergent-active compound, detergency builder and any other ingredients of doubtful compatibility with sodium percarbonate are excluded from the discrete region(s) in which the sodium percarbonate is segregated.

A preferred embodiment of the invention which is simple in structure and simple to manufacture is a tablet consisting of two layers: the first layer containing the percarbonate, and the second layer containing other ingredients. The percarbonate may be segregated alone, or together with one or more other ingredients that are fully compatible with it. It is generally preferred that a major proportion of the non-percarbonate ingredients should be separated from the percarbonate.

However, the stability of the percarbonate may actually be increased by segregating it together with a diluent in the form of a compatible inorganic salt. The salt is preferably in a finely divided or highly porous form, having a preferred surface area, as measured using nitrogen absorption, of 5-15 m^2/g. It is believed that it contributes to percarbonate stability by acting as a moisture sink. One especially preferred inorganic salt is sodium carbonate, which of course also plays a useful role in the detergent composition as a whole, as a detergency builder and provider of alkalinity. It is believed that sodium carbonate may also contribute to percarbonate stability by reabsorption of any liberated hydrogen peroxide.

According to one especially preferred embodiment of the invention, the diluent is in the form of a spray-dried composition comprising the compatible inorganic salt, more preferably sodium carbonate, and a polymeric binder.

The binder must itself be stable to oxidation. Preferred binders are acrylic and/or maleic polymers, for example, the acrylic/maleic copolymer sold commercially as Sokalan (Trade Mark) CP5 ex BASF. As well as their binder function which improves tablet integrity and allows tabletting without having to wet the percarbonate to any significant degree, polycarboxylate polymers of this type also have a useful detergency building and anti-redeposition action.

In this embodiment of the invention, the discrete tablet region or layer is the compaction product of a particulate composition prepared by mixing sodium percarbonate with the spray-dried salt/polymeric binder granules. This particulate starting composition suitably contains from 30 to 70 wt% of sodium percarbonate, from 30 to 70 wt% of the inorganic salt (preferably sodium carbonate), and from 0.5 to 5 wt% of the polymeric binder.

Detergent-active compounds

In a tablet intended to provide a fully-formulated bleaching detergent composition, detergent-active compounds are suitably present in an amount of from 2 to 50 wt%, more preferably from 5 to 40 wt%. Detergent-active material present may be anionic (soap or non-soap), cationic, zwitterionic, amphoteric, nonionic, or any combination of these.

Anionic detergent-active compounds may be present in an amount of from 2 to 40 wt%, preferably from 4 to 30 wt%.

Synthetic anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkyl sulphates, particularly sodium C_{12}-C_{15} primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rapeseed oil.

Anionic surfactants are preferably concentrated in discrete domains as described and claimed in our copending British Patent Application No 90 15504.5 (Unilever PLC).

Suitable nonionic detergent compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide.

Specific nonionic detergent compounds are alkyl (C_{6-22}) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic C_{8-20} primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long-chain tertiary amine oxides, tertiary phosphine oxides, and dialkyl sulphoxides.

Especially preferred are the primary and secondary alcohol ethoxylates, especially the C_{12-15} primary and secondaiy alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

The nonionic detergent-active compounds are preferably concentrated in discrete domains. Since the nonionic detergent compounds are generally liquids, these domains are preferably formed from any of the well-known carriers in the detergent business impregnated by nonionic detergent-active compound. Preferred carriers include zeolite; zeolite granulated with other materials, for example, Wessalith CS (Trade Mark), Wessalith CD (Trade Mark), Vegabond GB (Trade Mark), sodium perborate monohydrate; Burkeite (spray-dried sodium carbonate and sodium sulphate as disclosed in EP 221 776A (Unilever)).

Nonionic detergent-active compounds may optionally be mixed with materials which make the granules slow wetting and/or prevent the nonionic leaching out into the main tablet matrix. Such materials may suitably be fatty acids, especially lauric acid.

Detergency builders

Fully-formulated detergent tablets in accordance with the invention may suitably contain one or more detergency builders, preferably in an amount of from 5 to 80 wt%, more preferably from 20 to 80 wt%.

Preferred detergency builders are alkali metal aluminosilicates. However, these builders have a particular tendency to destabilise sodium percarbonate: therefore, in tablets of the invention containing sodium percarbonate segregation of these two components is essential.

Alkali metal (preferably sodium) aluminosilicates may suitably be incorporated in amounts of from 5 to 60% by weight (anhydrous Psis) of the composition, and may be either crystalline or amorphous or mixtures thereof, having the general formula:

$$0.8\text{-}1.5\ Na_2O.\ Al_2O_3.0.8\text{-}6\ SiO_2$$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof. Also of interest is the novel zeolite P described and claimed in EP 384 070A (Unilever).

Other builders may also be included in the detergent tablet of the invention if necessary or desired: suitable

organic or inorganic water-soluble or water-insoluble builders will readily suggest themselves to the skilled detergent formulator. Inorganic builders that may be present include alkali metal (generally sodium) carbonate; while organic builders include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates; and organic precipitant builders such as alkyl- and alkenylmalonates and succinates, and sulphonated fatty acid salts.

Especially preferred supplementary builders are polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%; and monomeric polycarboxylates, more especially citric acid and its salts, suitably used in amounts of from 3 to 20 wt%, more preferably from 5 to 15 wt%. As previously indicated, at least part of any polymer required in the formulation may be incorporated, as binder, in the region of the tablet in which the sodium percarbonate is segregated.

Preferred tabletted compositions of the invention preferably do not contain more than 5 wt% of inorganic phosphate builders, and are desirably substantially free of phosphate builders. However, phosphate-built tabletted compositions are also within the scope of the invention.

Enzymes

Fully-formulated tablets in accordance with the invention may also contain one of the detergency enzymes well-known in the art for their ability to degrade and aid in the removal of various soils and stains. Most enzymes are bleach-sensitive to some extent, and should also be excluded from the region containing the sodium percarbonate.

Suitable enzymes include the various proteases, cellulases, lipases, amylases, and mixtures thereof, which are designed to remove a variety of soils and stains from fabrics. Examples of suitable proteases are Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), Esperase (Trade Mark) and Savinase (Trade-Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark. Detergency enzymes are commonly employed in the form of granules or marumes, optionally with a protective coating, in amounts of from about 0.1% to about 3.0% by weight of the composition; and these granules or marumes present no problems with respect to compaction to form a tablet.

Minor ingredients

Fully-formulated tablets in accordance with the invention may also contain a fluorescer (optical brightener), for example, Tinopal (Trade Mark) DMS or Tinopal CBS available from Ciba-Geigy AG, Basel, Switzerland. Tinopal DMS is disodium 4,4'bis-(2-morpholino-4-anilino-s-triazin-6- ylamino) stilbene disulphonate; and Tinopal CBS is disodium 2,2'-bis-(phenyl-styryl) disulphonate.

An antifoam material is advantageously included in the fully-formulated tablet of the invention, especially if the tablet is primarily intended for use in front-loading drum-type automatic washing machines. Suitable antifoam materials are usually in granular form, such as those described in EP 266 863A (Unilever). Such antifoam granules typically comprise a mixture of silicone oil, petroleum jelly, hydrophobic silica and alkyl phosphate as antifoam active material, sorbed onto a porous absorbent water-soluble carbonate-based inorganic carrier material. Antifoam granules may be present in any amount up to 5% by weight of the composition.

It may also be desirable to include in the fully-formulated detergent tablet of the invention an amount of an alkali metal silicate, particularly sodium ortho-, meta- or preferably neutral or alkaline silicate. The presence of such alkali metal silicates at levels, for example, of 0.1 to 10 wt%, may be advantageous in providing protection against the corrosion of metal parts in washing machines, besides providing some measure of building and giving processing benefits.

Further ingredients which can optionally be employed in the fully-formulated detergent tablet of the invention include antiredeposition agents such as sodium carboxyethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl cellulose; fabric-softening agents; heavy metal sequestrants such as EDTA; perfumes; pigments, colorants or coloured speckles; and inorganic salts such as sodium and magnesium sulphate. Sodium sulphate may if desired be present as a filler material in amounts up to 40% by weight of the composition; however as little as 10% or less by weight of the composition of sodium sulphate, or even none at all, may be present.

As well as the functional detergent ingredients listed above, there may be present various ingredients specifically to aid tabletting or to aid tablet dispersion in the wash, for example, binders, disintegrants, or lubricants. As already indicated, some ingredients may give both functional wash benefits and tabletting benefits.

Tabletting

As previously indicated, the tablets of the invention are prepared by compaction of particulate starting material. Any suitable compacting process may be used, for example, tabletting, briquetting or extrusion, but tabletting is generally preferred.

For any given starting composition, the time taken for the tablet to disintegrate in the wash liquor will vary with the compaction pressure used to form the tablet. If the compaction pressure is too low, the tablet will tend to crumble and break up in the dry state, on handling and packaging; an increase in compaction pressure will improve tablet integrity, but eventually at the expense of disintegration time in the wash liquor.

Using an Instron (Trade Mark) Universal Testing Machine at constant speed, or a Research and Industrial screw hand press, to operate a steel punch and die, it has been found that effective tablets may be produced using compaction pressures ranging from 0.1 to 500 MPa (0.01 to 50 kN/cm^2), especially from 0.2 to 100 MPa (0.02 to 10 kN/cm^2).

The optimum compaction pressure will depend to some extent on the starting composition; for example, a tablet containing only the bleach composition of the invention may require a higher compaction pressure than that required for a fully formulated detergent composition tablet; a formulation containing a high proportion of organic ingredients (for example, surfactants) and a low proportion of inorganic salts may require a compaction pressure lower than that required for a formulation containing a lower proportion of organic ingredients and a higher proportion of inorganic salts; and a dry-mixed formulation will generally require a higher pressure than will a spray-dried powder.

Preferred tablet forms

Preferred tablets having improved disintegration and dissolution properties are described and claimed in our copending British Patent Applications Nos 90 15503.7 and 90 15504.5 (Unilever PLC) filed on 13 July 1990, and our copending British Patent Application filed on 1 July 1991 (Unilever PLC). These preferred tablet forms have particular relevance for tablets of fully formulated detergent compositions.

The tablet described and claimed in Application No. 90 15503.7 or a discrete region thereof, consists essentially of a matrix of particles substantially all of which have a particle size within a range having upper and lower limits each lying within the range of from 200 to 2000 μm and differing from each other by not more than 700 μm.

According to Application No. 90 15504.5, a tablet of compacted particulate detergent composition comprises a minor proportion (2-40 wt%) of a first component (a) which contains 20-100 wt% anionic surfactant, the rest of the composition containing only 0-3 wt% anionic surfactant.

The tablet described and claimed in our British application filed on 1 July 1991, or a discrete region thereof, consists essentially of a matrix of particles substantially all of while have a particle size >200μm, at least the particles of detergent-active compound and detergent builder are coated with binder/disintegrant before tablet compaction.

Dosage forms

The tablet of the invention may provide a bleaching composition for treating fabrics in the washing machine. This tablet may preferably be used as one of two or more tablets within a two-tablet or multi-tablet detergent system. Especially preferred is a two-tablet system in which the second tablet containing the detergent base system.

Alternatively, the detergent tablet of the invention may be formulated for use as a complete heavy-duty fabric washing composition. The consumer does not need to use a mix of tablets having different compositions.

Although one fully-formulated or bleach-only tablet may contain sufficient of all the components to provide the correct amount required for an average washload, it is convenient if each tablet contains a submultiple quantity of the composition required for average washing conditions, so that the consumer may vary the dosage according to the size and nature of the washload. For example, tablet sizes may be chosen such that two fully-formulated or bleach-only tablets are sufficient for an average washload; one or more further tablets may be added if the washload is particularly large or soiled; and one only tablet may be used if the load is small or only lightly soiled.

Alternatively, larger subdivisible full-formulated or bleach-only tablets representing a single or multiple dose may be provided with scorings or indentations to indicate unit dose or submultiple unit dose size to the consumer and to provide a weak point to assist the consumer in breaking the tablet if appropriate.

The size of the tablet will suitably range from 5 to 160 g, depending on the wash conditions under which

it is intended to be used; whether it is a bleach-only tablet or contains other ingredients; and whether it represents a single dose, a multiple dose or a submultiple dose. Bleach-only tablets preferably range from 5 to 50 g in size. Fully formulated tablets preferably range from 10 to 160 g in size, more preferably from 15 to 60 g in size.

The tablet may be of any suitable shape, but for manufacturing and packaging convenience is preferably of uniform cross-section, for example, circular (preferred) or rectangular.

EXAMPLES

The following non-limiting Examples illustrate the invention. Parts and percentages are by weight unless otherwise stated. Examples identified by numbers are in accordance with the invention, while Examples identified by letters are comparative.

Examples 1 to 3

Measurement of the observed pseudo-first order perhydrolysis rate constant

A 4.1mM solution of sodium perborate tetrahydrate was prepared at 30°C and buffered to pH 10 with (25mM) sodium carbonate buffer.

2.1/n mM of activator, where n is the number of perhydrolysable groups on the activator, was added neat (ie not in solution) to the predissolved perborate.

The peracid yields were measured using a sodium thiosulphate titration at 0°C (standard acid/ice method).

The observed pseudo-first-order perhydrolysis rate constant (K_{obs}) was measured for the following activators:

sodium benzoyloxy benzenesulphonate (SBOBS) - Example 1;

TAED - Example 2;

glycerol triacetate (GTA) - Example 3.

Results are shown in Table 1.

Table 1

Example	Activator	K_{obs} (s^{-1})
1	SBOBS	3.0×10^{-2}
2	TAED	2.3×10^{-3}
3	GTA	1.9×10^{-4}

Examples 4 to 6, Comparative Examples A to C

(i) Preparation of bleach compositions

A 40 wt% solution of Analar sodium carbonate was prepared. Acrylic/maleic copolymer in sodium salt form - Sokalan (Trade Mark) CP5 ex BASF - was admixed in an amount of 2 wt% based on the sodium carbonate (dry weight), and the solution was stirred at 50°C for 2 hours. The solution was then spray-dried using laboratory equipment (inlet temperature 275°C, feed rate 10 ml/min through a 0.75 mm jet) to give granular anhydrous sodium carbonate of high specific surface area.

Bleach compositions were then prepared by dry-mixing the spray-dried sodium carbonate composition with sodium percarbonate and bleach activator to give the formulations shown in Table 2. The bleach activators used

were TAED (in granule form), glycerol triacetate (GTA), and sodium benzoyloxy benzenesulphonate (SBOBS), used in amounts chosen to give equivalent weights of peracid (assuming 100% peracid generation efficiency). The GTA, being a liquid, was preabsorbed in the spray-dried sodium carbonate.

(ii) Preparation of detergent base composition

A detergent base composition was prepared to the formulation shown in Table 2, by spray-drying an aqueous slurry of all ingredients except the nonionic surfactant 7EO which was subsequently sprayed on.

(iii) Tabletting

Tablets were prepared using an Instron (Trade Mark) Model 4202 Materials Testing Machine fitted with a 10KN load cell.

For Examples 4 to 6 (the invention), bleach compositions (10 g) was added to the die, the die was tapped gently to level the powder, and detergent base composition (30 g) was added on top of the bleach composition, before tabletting.

The tablets each weighed 40 g, and were 53 mm in diameter and 22 mm in thickness.

Comparative Examples A, B and C were loose powders of the same composition, prepared by mixing the bleach composition and the detergent base composition in the same proportions as in Example 4.

(iv) Bleaching performance

Bleaching performance was assessed by measuring the increase in reflectance at 460 nm (with incident light <400 nm filtered out) (δR_{460}) of standard tea-stained test cloths after washing in a Miele (Trade Mark) 756 front-loading automatic washing machine, using a standard heat-up to 40°C wash in the presence of a 1 kg ballast washload. For each wash two tablets (Examples 4 to 6) or 80 g of powder (Comparative Examples A to C) were used. The results are shown in Table 3.

Table 2 Detergent Base and Tablet Compositions

	% (base)	% (tablet)
Detergent base composition		
Linear alkylbenzene sulphonate	9.60	7.20
Nonionic surfactant (7EO)	4.10	3.08
Soap	2.60	1.95
Zeolite 4A (anhydrous basis)	40.50	30.38
Polymer (acrylic/maleic)	6.10	4.58
Sodium alkaline silicate	0.70	0.53
Sodium carbonate	14.80	11.10
Sodium carboxymethylcellulose	0.90	0.68
Minor ingredients	2.70	2.03
Moisture	18.00	13.50
	100.00	75.00

Tablet and Powder Compositions

	4,A	5,B	6,C
Detergent base composition	75.0	75.0	75.0
Sodium percarbonate	12.5	12.5	12.5
Spray-dried sodium carbonate	10.25	9.5	7.65
TAED granules (82% active)	2.25	-	-
GTA	-	3.0	-
SBOBS	-	-	4.85
	100.0	100.0	100.0

Table 3 Bleach Performance Results

Example	Activator	Reflectance increase (δR_{460*}) Tablet	Powder
4	TAED	9.3	
A	TAED		5.4
5	GTA	7.1	
B	GTA		5.9
6	SBOBS	13.6	
C	SBOBS		11.0

Example 7, Comparative Example D

(i) Preparation of bleach compositions

A spray-dried sodium carbonate composition was prepared as described for Examples 4 to 6. Bleach compositions were then prepared by dry-mixing the spray-dried sodium carbonate composition with sodium percarbonate, 1-O-octanoyl-2,3,4,6-tetra-O-acetyl glucose (OTAG) and glycerol as shown in Table 4.

Table 4

Component	%(wt) (tablet)
OTAG	9.4
Sodium percarbonate	42.9
Spray-dried sodium carbonate composition	42.9
Glycerol	4.8
	100.0

(ii) Tabletting

Tablets were prepared using an Instron (Trade Mark) Model 4202 Materials Testing Machine fitted with a 5KN load cell.

The tablets each weighed 25.62 g and were 40 mm in diameter and 13 mm in thickness.

Comparative Example D was a loose powder of the same composition.

(iii) Bleaching performance

Bleaching performance was assessed by measuring the increase in reflectance at 460 nm (with incident light <400 nm filtered out) (δR_{460^*}) of standard tea-stained test cloths after washing in a Miele (Trade Mark) 756 front-loading washing machine, in 10 litres of soft water in the presence of a buffer containing 10g/l sodium metaborate and 5g/l sodium bicarbonate at pH 9.85 at 20°C for 30 minutes. For each wash one tablet (Example 7) or 25.8g of powder (Comparative Example D) were used. The results are shown in Table 5.

Table 5

Example	Reflectance Increase (δR_{460^*})
7	3.8
D	2.4

Example 8, Comparative Examples E and F

(i) Preparation of bleach compositions

A spray-dried sodium carbonate composition was prepared as described for Examples 4 to 6. Bleach compositins were then prepared by dry-mixing the spray-dried sodium carbonate composition with sodium percarbonate and OTAG as shown in Table 6.

Table 6

Component	%(wt) (tablet)
OTAG	10.6
Sodium percarbonate	44.7
Spray-dried sodium carbonate composition	44.7
	100.0

(ii) Tabletting

Tablets were prepared as described for Example 7.
Comparative Examples E and F were loose powders of the same composition.

(iii) Preparation of detergent base powder composition

A detergent base composition was prepared to the formulation shown in Table 7, by spray-drying an aqueous slurry of all ingredients except the nonionic surfactant 7EO which was subsequently sprayed on.

Table 7, Detergent Base Powder Composition

Detergent base composition	% (base)
Linear alkylbenzene sulphonate	10.00
Nonionic surfactant (7EO)	4.58
Soap	2.76
Zeolite 4A (anhydrous basis)	41.79
Polymer (acrylic/maleic)	4.47
Sodium alkaline silicate	0.68
Sodium carbonate	18.13
Sodium carboxymethylcellulose	0.84
Fluorescer	0.33
Moisture	16.42
	100.00

(iv) Bleaching performance

Bleaching performance was assessed by measuring the increase in reflectance at 460 nm (with incident light >400 nm filtered out) (δR_{460}) of both standard tea-stained test cloths and EMPA wine stained cloths after washing in a Miele (Trade Mark) 756 front-loading machine, in 10 litres of water at 40°C. For each wash one tablet (Example 8) or 25.8g of bleach composition powder (Comparative Examples E and F) were used in conjunction with 50g of the described detergent base powder. For Comparative Example E the bleach composition powder was added to 20 ml of water in a bottle and shaken vigorously for one minute for adding to the wash, thus enabling some perhydrolysis to take place under conditions of high concentration and pH prior to the bleach

performance test described above. The results are shown in Table 8.

Table 8

Example	Reflectance increase (δR_{460*}) Tea stain	Wine stain
8	6.2	17.9
E	3.8	12.8
F	2.0	11.3

Examples 9 to 13, Comparative Example G

The effect of tabletting pressure on peracid yield using the bleach composition of Example 3 (containing TAED as bleach activator) was investigated. The results are shown in Table 9.

For this work, separate bleach and detergent tablets were prepared, so that the bleach composition could be tabletted at a series of different pressures (0.4 to 8 KN/cm^2) while the detergent base powder was always tabletted at the same pressure (0.4 KN/cm^2), thus avoiding complications that would have arisen if the detergent base powder had dissolved at different rates in the different experiments.

In each experiment, two bleach composition tablets (each 10 g) and two detergent base composition tablets (each 30 g) were used.

Wash conditions, selected to obtain maximum reproducibility, were a long (45 minute) wash at ambient temperature in the Miele 756 washing machine in the absence of a ballast load.

Peracid yields, expressed as a percentage of the theoretical yield, were measured by a standard iodine/thiosulphate titration at 0°C at intervals throughout the wash: the maximum yield, and the time (T_{max}) taken to reach that maximum, were recorded.

The integrated yield (arbitrary units) was also calculated, by numerical integration of the peracid yield over the whole wash time: this is a measure of the peracid level available over the whole of the wash period.

Table 9: Peracid Yield Results (Sodium Percarbonate)

Example	Tabletting pressure (kN/cm^2)	Maximum yield (mole %)	T_{max} (min)	Integrated yield (arbitrary units)
G	0 (powder)	83	5	2965
9	0.4	80	10	2907
10	0.8	86	8	3060
11	1.6	88	12	3252
12	4.8	94	12	3458
13	8	86	14	3058

It may be seen that at the optimum (a tabletting pressure of 4.8 KN/cm) the integrated yield was just over 115% of that for the powdered formulation.

Examples 14 to 18, Comparative Example H

The procedure of Examples 9 to 13 and G was repeated using a bleach formulation containing sodium perborate tetrahydrate and TAED.

The formulation was adjusted slightly in order to maintain the same levels of available oxygen as in Examples 9 to 13 and G, since commercial sodium perborate tetrahydrate contains about 10% available oxygen while sodium percarbonate contains about 13.5%. This adjustment increased the weight of the bleach tablets from 10 g to 11.75 g, while the weight of the detergent tablets remained at 30 g. The bleach formulation was as follows:

Detergent base composition	71.9
Spray-dried sodium carbonate	9.8
Sodium perborate tetrahydrate	16.1
TAED granules (82% active)	2.2
	100.0

Again, two bleach tablets and two detergent tablets were used per wash.

The results are shown in Table 10. Some benefit was observed at higher tabletting pressures, but it was smaller than the benefit observed with sodium percarbonate.

Table 10: Peracid Yield Results (Sodium Perborate Tetrahydrate)

Example	Tabletting pressure (kN/cm^2)	Integrated yield (arbitrary units)
H	0 (powder)	2069
14	0.4	2180
15	0.8	2045
16	1.6	2097
17	4.8	2269
18	8	2251

Claims

1. A tablet of compressed particulate bleaching composition comprising a persalt and a bleach activator, optionally a detergent-active compound, a detergent builder and other detergent ingredients, characterised in that it contains a bleach activator having an observed pseudo-first order perhydrolysis rate constant (K_{obs}) of from 1.5×10^{-4} to 350×10^{-4} sec^{-1}; with the proviso that if the persalt is sodium perborate and the bleach activator is a N-diacylated or N,N'-polyacylated amine, the persalt is segregated from the bleach activator.

2. A tablet as claimed in claim 1 characterised in that it comprises a detergent-active compound and a detergency builder.

3. A tablet as claimed in claim 1 or claim 2, characterised in that the persalt is sodium percarbonate.

4. A tablet as claimed in claim 3, characterised in that the sodium percarbonate is separated from any ingredient of the composition detrimental to its stability by segregation in a discrete region of the tablet.

5. A tablet as claimed in any preceding claim, characterised in that the bleach activator is a peracetic acid precursor.

6. A tablet as claimed in claim 5, characterised in that the bleach activator is tetraacetylethylenediamine.

7. A tablet as claimed in claim 5, characterised in that the bleach activator is glycerol triacetate.

8. A tablet as claimed in any one of claims 1 to 4, characterised in that the bleach activator is a perbenzoic

acid precursor.

9. A tablet as claimed in claim 8, characterised in that the bleach activator is sodium benzoyloxy benzene sulphonate.

10. A tablet as claimed in any one of claims 1 to 4, characterised in that the bleach activator is 1-O-octanoyl-2,3,4,6-tetra-O-acetyl glucose.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9597

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 312 278 (UNILEVER PLC) * page 2, line 55; page 3, lines 1-8; page 5, lines 46,53-55; page 6, lines 3-7,43-46; page 12, table 6, example 7B * ---	1-3	C 11 D 17/00 C 11 D 3/39
A	FR-A-2 236 930 (HENKEL & CIE GMBH) * page 2, lines 10-21; page 3; page 4, lines 1-18; page 8, lines 16-21 * ---	1-4,6,8-10	
D,A	GB-A- 911 204 (UNILEVER LTD) * claims * -----	1,4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	13-01-1992	PELLI-WABLAT B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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